THE LIQUIDUS SURFACE IN THE $Al_2O_3 - ZrO_2 - Y_2O_3$ PHASE DIAGRAM

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The structure of the bounding binary systems has been examined in some detail. The phase diagram for the $Al_2O_3 - ZrO_2$ system is of simple eutectic type [1-5]. Solubility on the basis of α-Al_2O_3 (subsequently just Al_2O_3) is virtually absent. In the region of high ZrO_2 contents above 2260°C, solid solutions are formed on the basis of ZrO_2 having a structure of fluorite type F. The solubility of Al_2O_3 in the cubic modification F is not more than 5 mole.%. Below 2260°C, there is a narrow field of solid solutions having the tetragonal ZrO_2 structure (T). The liquidus is characterized by a metatectic transformation (F $\rightleftarrows$ T + L; 80% (mol.) ZrO_2; 2260°C) and the eutectic one (L $\rightleftarrows$ T + Al_2O_3; 37% (mol.) ZrO_2; 1860°C). The $ZrO_2 - Y_2O_3$ system at high temperatures is one with restricted mutual solubility of the components in the solid state [6-8]. Solid solutions F are formed at 2450°C with a limit on the Y_2O_3 content of 54 mole.%. Yttrium oxide crystallizes in two
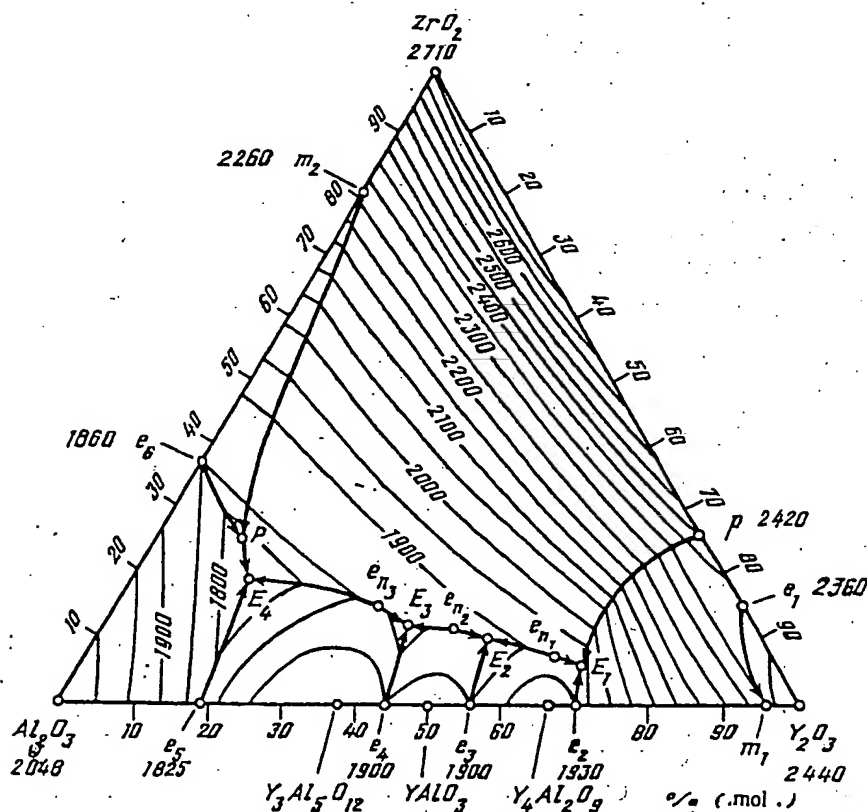

Fig. 1. Projection of the liquidus surface in the phase diagram for the $Al_2O_3 - ZrO_2 - Y_2O_3$ system on the plane of the concentration triangle.
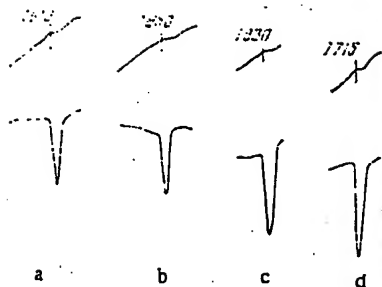
Fig. 2
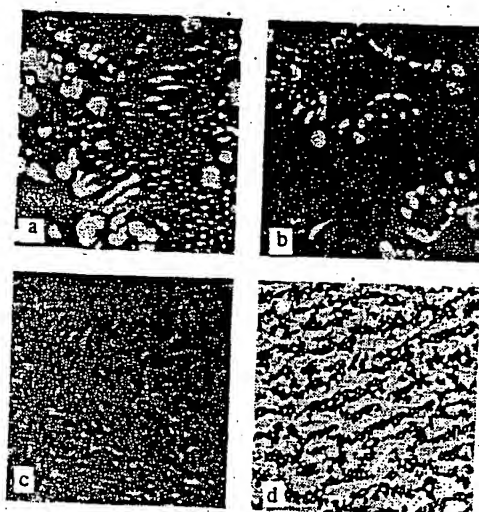

Fig. 3

Fig. 2. Heating curves for ternary eutectic alloys in the $Al_2O_3-ZrO_2-Y_2O_3$ system. Here and in Fig. 3, the compositions of the alloys in mole.% are: a) 62 Al_2O_3 + 6 ZrO_2 + 68 $Y_2O_3(E_1)$; b) 37 Al_2O_3 + 10 ZrO_2 + 53 Y_2O_3 (E_2); c) 47 Al_2O_3 + 12 ZrO_2 + 41 Y_2O_3 (E_3); d) 65 Al_2O_3 + 19 ZrO_2 + 16 Y_2O_3 (E_4).

Fig. 3. Electron micrographs of ternary eutectic alloys in the $Al_2O_3-ZrO_2-Y_2O_3$ system; magnifications: 500 (a), 700 (b). and 3000 (c and d).

polymorphic forms (the C and H types of REE oxides), and there are solid-solution regions based on these. The liquidus is characterized [8] by a eutectic transformation (L $\rightleftarrows$ F + H; 15% (mol.) ZrO_2; 2360°C) and a peritectic one (L + F $\rightleftarrows$ C; 26% (mol.) ZrO_2; 2450°C) (points e_1 and p respectively). Three congruently melting compounds are formed in the $Al_2O_3-Y_2O_3$ system: $Y_3Al_5O_{12}$ (Y_3A_5), $YAlO_3$ (YA) and $Y_4Al_2O_9$ (Y_2A), whose melting points are 1950, and 1980°C respectively [5, 9-16]. Eutectic-point coordinates: $Y_2O_3-Y_2A$ (e_2) — 1930°C, 29.5% (mol.) Al_2O_3; Y_2A-YA (e_3) — 1900°C, 44% (mol.) Al_2O_3; $YA-Y_3A_5$ (e_4) — 1900°C, 56% (mol.) Al_2O_3; $Y_3A_5-Al_2O_3$ (e_5) — 1825°C, 76% (mol.) Al_2O_3. The system also shows the metatectic transformation H $\rightleftarrows$ C + L at 2350°C, which is reflected on the liquidus as point m_1 at an Al_2O_3 content of 4 mole.% and which corresponds to transformation in the yttrium oxide (H $\rightleftarrows$ C) [5].

The interactions in the $Al_2O_3-ZrO_2-Y_2O_3$ system have not been studied adequately. Isothermal sections have been constructed at 1250, 1450, 1600, 1650, and 1800°C [17-20], and also in part the quasibinary sections [5], for which the liquidus is characterized by the primary crystallization fields for the F solid solutions for the various contents of Y_2O_3 and Y_3A_5 or YA and Y_2A respectively. The following are the coordinates of the eutectic points (e_{n_1}, e_{n_2}, and e_{n_3} are saddle points for the ternary system): 7.5% (mol.) ZrO_2, 1940°C; 11.5% (mol.) ZrO_2, 1870°C; 15.0% (mol.) ZrO_2, 1865°C.

We have examined the liquidus surface for the $Al_2O_3-ZrO_2-Y_2O_3$ phase diagram, which is of interest for making constructional ceramic materials. The methods of making and testing the specimens have been described in [5].

Figure 1 shows that this surface in the $Al_2O_3-ZrO_2-Y_2O_3$ system is formed by eight fields for primary crystallization. The polymorphism in ZrO_2 (F, T) and Y_2O_3 (H, C) makes itself felt as four primary crystallization fields. The monoclinic form of ZrO_2 does not have its own primary crystallization field on the liquidus because its temperatures are low by comparison with those of the binary and ternary eutectics. The fields for the primary crystallization of the T and H solid solutions are small and are bounded by the m_2Pe_6 and e_1m_1 curves respectively. The field for solid solutions based on the C form of Y_2O_3 is fairly wide and is bounded by the curves pE_1e_2 and e_1m_1. Much of the area in the liquidus surface is occupied by the primary crystallization field for F solid solutions based on ZrO_2, which is bounded by the envelope $m_2PE_4e_{n_3}E_3e_{n_2}E_2e_{n_1}E_1p$, which reflects the high thermodynamic stability of that phase. The surface for the primary crystallization of F intersects the analogous fields for the other phases along the curves for the binary crystallization of the corresponding eutectics, which run near the $Al_2O_3-Y_2O_3$ side in the composition triangle, apart from the curve for the joint crystallization of F + T. The solid solution with the fluoride-type structure F is in equilibrium with all the phases in the system

Equilibrium points	Temperature, °C	Composition, mole.%			Nonvariant equilibrium
		Al_2O_3	ZrO_2	Y_2O_3	
E_1	1910	26	6	68	$L_{E_1} \rightleftharpoons Y_2A + F + C$
E_2	1850	37	10	53	$L_{E_2} \rightleftharpoons YA + F + Y_4A$
E_3	1800	47	12	41	$L_{E_3} \rightleftharpoons Y_3A_5 + F + YA$
E_4	1715	65	19	16	$L_{E_4} \rightleftharpoons Al_2O_3 + F + Y_3A_5$
P	1745	63	25	12	$L_P + T \rightleftharpoons F + Al_2O_3$

apart from the H solid solutions and interacts with them on a eutectic mechanism, apart from the peritectic reaction $L + T \rightleftharpoons F + A$. The metatectic process $F \rightleftharpoons T + L$ (m_2) becomes peritectic in the ternary system: $L + T \rightleftharpoons F + A$. Table 1 gives the coordinates of the nonvariant points in the $Al_2O_3 - ZrO_2 - Y_2O_3$ system.

Table 1 and Fig. 1 show that the liquidus surface has five four-phase nonvariant equilibria (four relate to the eutectic type and one to the peritectic type) and three three-phase ones for quasibinary eutectics.

Figure 2 shows DTA curves, which indicate the nonvariant transformations in the $Al_2O_3 - ZrO_2 - Y_2O_3$ system, while Fig. 3 shows the microstructures corresponding to the nonvariant points. The minimum melting temperature is 1715°C and relates to the ternary eutectic E_4. Here we note that the isothermal section for the system at 1800°C constructed in [18] is erroneous because the liquid phase field appears in the system at that temperature, and also the liquid phase in equilibrium with F, Al_2O_3, and Y_3A_5 crystals. The maximal liquidus temperature is equal to the melting point of the alloy containing 80 mole.% ZrO_2 in the $ZrO_2 - Y_2O_3$ system (2775°C). We did not observe the new phases or regions of ternary solid solutions in the $Al_2O_3 - ZrO_2 - Y_2O_3$ system, which means that materials in the ternary system can be used to realize the unique properties of the M, T, and F solid solutions based on ZrO_2 in combination with the properties of the other phases.

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